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Page IFC

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Chu-Wen Yang, Sen-Lin Tang, Ling-Yun Chen, Bea-Ven Chang
Pages 9-17

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Influence of fibre architecture on the biodegradability of FLAX/PLA composites

Thomas Bayerl, Markus Geith, Arcot A. Somashekar, Debes Bhattacharyya
Pages 18-25

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Purification and characterization of four key enzymes from a feather-degrading *Bacillus subtilis* from the gut of tarantula *Chilobrachys guangxiensis*

Qingyang Liu, Tiehan Zhang, Nan Song, Qian Li, ... Jinjun Chen
Pages 26-32

Purchase PDF Article preview

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Microcosmic study of endosulfan degradation by *Paenibacillus* sp. ISTP10 and its toxicological evaluation using mammalian cell line

Moni Kumari, Pooja Ghosh, Swati, Indu Shekhar Thakur
Pages 33-40

Purchase PDF Article preview

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Effects of substratum type on bacterial community structure in biofilms in relation to settlement of plantigrades of the mussel *Mytilus coruscus*

Yi-Feng Li, Yu-Ru Chen, Jin-Long Yang, Wei-Yang Bao, ... De-Wen Ding
Pages 41-49

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Webbing clothes moth catch and the management of heritage environments

Peter Brimblecombe, Pascal Querner

Pages 50-57

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Short communication ○ Abstract only

Reducing ammonia volatilization during composting of organic waste through addition of hydrothermally treated lignocellulose

Bakhtiyor Nakhshiniev, Chamila Perera, Muhammad Kunta Biddinika, Hazel Bantolino Gonzales, ... Kunio Yoshikawa

Pages 58-62

Purchase PDF Article preview

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Evaluation of the microbial community of upflow anaerobic sludge blanket reactors used for the removal and degradation of linear alkylbenzene sulfonate by pyrosequencing

Dagoberto Y. Okada, Tiago P. Delforno, Claudia Etchebehere, Maria B.A. Varesche

Pages 63-70

Purchase PDF Article preview

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Characterization of the bacterial communities and iron corrosion scales in drinking groundwater distribution systems with chlorine/chloramine

Xiaoxiao Li, Haibo Wang, Yu Zhang, Chun Hu, Min Yang

Pages 71-79

Purchase PDF Article preview

Research article ○ Abstract only

Aerobic removal of methoxychlor by a native *Streptomyces* strain: Identification of intermediate metabolites

Natalia Bourguignon, María S. Fuentes, Claudia S. Benimeli, Sergio A. Cuozzo, María J. Amoroso

Pages 80-86

Purchase PDF Article preview

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Testing the antibacterial activity of doped TiO_2 for preventing biodeterioration of cultural heritage building materials

Mauro F. La Russa, Andrea Macchia, Silvestro A. Ruffolo, Filomena De Leo, ... Clara Urzì

Pages 87-96

Purchase PDF Article preview

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Biodegradation of wood exposed in the marine environment: Evaluation of the hazard posed by marine wood-borers in fifteen European sites

L.M.S. Borges

Pages 97-104

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Ferric biogenic flocculant produced by *Acidithiobacillus ferrooxidans* enable rapid dewaterability of municipal sewage sludge: A comparison with commercial cationic polymer

Mayur B. Kurade, Kumarasamy Murugesan, Ammaiyappan Selvam, Shuk-Man Yu, Jonathan W.C. Wong

Pages 105-111

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Development of low cost upflow column bioreactor for degradation and detoxification of Blue HERD and textile effluent by *Lysinibacillus* sp. RGS immobilized on Loofa

Priyanka A. Bedekar, Rijuta G. Saratale, Ganesh D. Saratale, Sanjay P. Govindwar

Pages 112-120

Purchase PDF Article preview

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Parameter determination involved in phytotoxicity and transport of cadmium in rice seedlings

Xue-Hong Zhang, Xiao-Zhang Yu, Yan-Peng Liang

Pages 121-126

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Efficient biodegradation of quinolone – Factors determining the process

Aleksandra Felczak, Katarzyna Zawadzka, Katarzyna Lisowska

Pages 127-134

Purchase PDF Article preview

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Microbially enhanced oil recovery from miniature model columns through stimulation of indigenous microflora with nitrate

Yuriy Kryachko, Gerrit Voordouw

Pages 135-143

Purchase PDF Article preview

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Seaweed (*Eucheuma cottonii*) associated microorganisms, a versatile enzyme source for the lignocellulosic biomass processing

Velayudhan Satheeja Santhi, Ashok Kumar Bhagat, Somasundaram Saranya, Ganesan Govindarajan, Solomon Robinson David Jebakumar

Pages 144-151

Purchase PDF Article preview

Research article ○ Abstract only

The effect of trace elements on wheat straw degradation by *Trametes gibbosa*

Aleksandar Knežević, Mirjana Stajić, Jelena Vukojević, Ivan Milovanović

Pages 152-156

Purchase PDF Article preview

Review article ○ Abstract only

Biological colonization patterns on the ruins of Angkor temples (Cambodia) in the biodeterioration vs bioprotection debate

F. Bartoli, A. Casanova Municchia, Y. Futagami, H. Kashiwadani, ... G. Caneva

Pages 157-165

Purchase PDF Article preview

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Biodegradation of bisphenol A by bacterial consortia

Er Jin Eio, Minako Kawai, Kenji Tsuchiya, Shuichi Yamamoto, Tatsuki Toda
Pages 166-173

Purchase PDF Article preview

Research article ○ Abstract only

Characterization of fungi of the genus *Mycena* isolated from houses thatched with *Phragmites communis* Trin. in Northern Germany: Enzyme pattern and reed decay

Rovena Dosdall, Veronika Hahn, Franziska Preuß, Hanns Kreisel, ... Frieder Schauer
Pages 174-180

Purchase PDF Article preview

Review article ○ Abstract only

Chromium removal in constructed wetlands: A review

Mar-Yam Sultana, Christos S. Akratos, Stavros Pavlou, Dimitrios V. Vayenas
Pages 181-190

Purchase PDF Article preview

Short communication ○ Abstract only

Saccharomyces pastorianus immobilized on brewer's spent grain in continuous system for lead ion biosorption

Edyta Kordialik-Bogacka
Pages 191-197

Purchase PDF Article preview

Short communication ○ Abstract only

Methanogenic potential of an anaerobic sludge in the presence of anionic and nonionic surfactants

Fabrício Motteran, Juliana Kawanishi Braga, Isabel Kimiko Sakamoto, Maria Bernadete Amâncio Varesche
Pages 198-204

Purchase PDF Article preview

Special Section: Special Issue: ISMOS-4

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Estuarine sediment hydrocarbon-degrading microbial communities demonstrate resilience to nanosilver

Jessica Beddow, Björn Stölpe, Paula A. Cole, Jamie R. Lead, ... Corinne Whitby

Pages 206-215

Download PDF Article preview

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(Per)chlorate reduction at high temperature: Physiological study of *Archaeoglobus fulgidus* and potential implications for novel souring mitigation strategies

M.G. Liebensteiner, A.J.M. Stams, B.P. Lomans

Pages 216-222

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Previous vol/issue Next vol/issue

ISSN: 0964-8305

International Biodeterioration & Biodegradation 96 (2014) 58–62

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Short communication

Reducing ammonia volatilization during composting of organic waste through addition of hydrothermally treated lignocellulose

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ABSTRACT

Composting of organic wastes rich in nitrogen suffers from the loss of certain amount of nitrogen into atmosphere, notably through ammonia (NH_3) volatilization. In this study, the addition of hydrothermally treated lignocellulose (180 °C, 1.0 MPa, 30 min) to composting mixture as a new strategy for reducing NH_3 volatilization during the bench-scale composting experiment was tested. The results show that the addition of hydrothermally treated lignocellulose is very effective in reducing NH_3 volatilization during composting process. The effect was mainly due to the presence of high amount of simple sugars in treated lignocellulose, which promoted microbial activity to immobilize more inorganic nitrogen during intensive decomposition of organic nitrogenous compounds. As a result, NH_3 volatilization reduced from 9.61% in Control to 3.37% in Treated composting mixture. The difference in NH_3 volatilization was also reflected by significant difference ($p < 0.05$) in C/N ratio of the final compost products: with 23.89 in Control and 19.47 in Treated compost.

Introduction

Composting is a simple and low-cost method to convert the organic wastes into safer and usable end product. If properly accomplished, composting stabilizes organic waste, kills pathogens and weeds, suppresses unpleasant odor, reduces the volume of the waste and turns it into a nutrient-rich product that can be used as organic fertilizer for plant growth. However, composting of organic wastes rich in nitrogen suffers from the loss of certain amount of nitrogen into atmosphere, notably through ammonia (NH_3) volatilization. The process is the result of activity of microorganisms on organic nitrogenous compounds that are faster in decomposition compared to organic carbon compounds (Bernal et al., 1993; Beline et al., 1998). Substantial loss of nitrogen through NH_3 volatilization, sometimes as high as 40–80% of the initial mass of nitrogen, has been reported previously in the literature (Kirchmann and Witter, 1989; Martins and Dewes, 1992; Kithome et al., 1999; Lee et al., 2009). The consequence of such massive NH_3 volatilization is not only the increase of air pollution but also the decrease of agronomic value of end product.

Several practices such as optimization of initial C/N ratio (Jiang et al., 2011), process temperature (Pagans et al., 2006; Eklind et al., 2007), pH (Nakasaki et al., 1993), aeration (DeGuardia et al., 2008) and moisture regime (Bueno et al., 2008; Jiang et al., 2011) have been found to influence the degree of NH_3 volatilization from compost. However, optimization of these parameters under the practical composting conditions is not always an easy task and moreover, does not always appear to be effective. Notable reductions of NH_3 volatilization and subsequent retention of nitrogen in the final compost product have been achieved after the addition of various mineral absorbents and acidifying agents to the compost (Bernal et al., 1993; Termeer and Warman, 1993; Mahimairaja et al., 1994; Prochnow et al., 1995; Kithome et al., 1999; Boucher et al., 1999; Jeong and Kim, 2001; Zhang and Lau, 2007; Alipour and Torkashvand, 2009). Unfortunately, mineral absorbents are not commonly available and application of acidifiers requires special

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precaution to avoid overdosing, which may conversely slow down the activity of the microorganisms and/or cause salinity problem (Zhang and Lau, 2007; Lee et al., 2009; Wang et al., 2013).

The simplest technique that could be used to suppress NH_3 volatilization effectively is to add simple sugars, e.g., the forms of carbon that is necessary for immediate immobilization of nitrogen and subsequent suppression of NH_3 volatilization (Reinertsen et al., 1984). Notable reduction in NH_3 volatilization was shown when the fresh hog manure was supplemented with glucose (Subair, 1995). Molasses, rich normally in sucrose, was applied to compost mixture and NH_3 volatilization was remarkably suppressed, which was caused by immobilization (Liang et al., 2006). In the experiments of Li et al. (2013a,b), the addition of sucrose and glucose to sewage sludge, straw and sawdust mixtures led to more than 55% reduction of NH_3 emissions. However, in order to reduce NH_3 volatilization effectively, large amount of expensive sugars must be added (Li et al., 2013a) and recently, application of molasses is becoming uneconomical due to its growing demand from the bio-ethanol production industries.

Previously, a novel hydrothermal treatment technology with mild reaction conditions (160 °C < T < 220 °C, 0.6 MPa < P < 2.4 MPa, 30 min) was investigated as a treatment step in enhancing biodegradability of lignocellulosic residues for organic fertilizer production (Nakhshiniev et al., 2012). Specifically, hydrothermal treatment was performed to disrupt hemicellulose–lignin association and improve susceptibility of cellulose fibers to microbial attack. According to the results, treatment temperature of 180 °C was the most favorable for accelerating aerobic degradation of lignocellulose, and that this improved biodegradability was mainly attributed to the effect of treatment on solubilization of the major portion of hemicellulose polysaccharides into simple sugars. Thus, it was hypothesized that the addition of hydrothermally treated lignocellulose as a carbon amendment might reduce NH_3 volatilization during composting process.

Material and methods

Material

In this research, freshly harvested green kudzu plant (*Pueraria montanavarlobata*) and bamboo tree (*Phyllostachys pubescens*) residues were used as the model composting ingredients. The green kudzu was used as a high-nitrogen material while bamboo was used as a lignocellulose carbon amendment. After the harvest, the residues were chopped into chips (2–3 cm) and oven-dried (55 °C) to constant weight. The oven-dried residues were then, grounded, sieved (<0.25 mm) and preserved for the next experimental procedures. The physicochemical properties of the materials are summarized in Table 1.

Table 1
Physicochemical properties of composting ingredients used in the present research.

Parameters (dry base)	Green kudzu	Raw bamboo	Treated bamboo
Simple sugars[a], %	10.61 (0.18)	1.36 (0.09)	15.70 (0.29)
Hemicellulose, %	18.42 (1.55)	30.83 (0.21)	7.48 (1.47)
Cellulose, %	26.15 (0.73)	38.01 (0.97)	39.22 (1.91)
Lignin, %	16.17 (0.82)	19.15 (0.76)	32.74 (0.44)
OM, %	91.93 (0.12)	98.30 (0.03)	97.02 (0.39)
Total C, %	44.61 (0.04)	47.50 (0.04)	51.30 (0.03)
Total N, %	3.74 (0.01)	0.41 (0.03)	0.44 (0.01)
C:N ratio	11.93	116.59	115.85

A (B), where A = mean and (B = standard deviation) with n = 3.
[a] As a glucose and xylose equivalent.

Hydrothermal treatment of bamboo

Hydrothermal treatment of bamboo was conducted in a 0.5 l batch-type hydrothermal reactor (MMJ-500, Japan) equipped with automated stirrer, pressure sensor and temperature controller. The schematic diagram of the experimental set-up was reported previously (Nakhshiniev et al., 2012). The amount of grounded residue and water mixture loaded into the reactor was about 60 g, corresponding to 1:3 mixing ratio. The reactor was then heated to 180 °C (1.0 MPa) at an average heating rate of 7.2 °C/min and a constant stirring speed of 200 rpm. In order to prevent combustion during heating, the air inside the reactor was initially evacuated with a stream of argon gas. After reaching the pre-set temperature, the mixture was further held in the reactor for 30 min. Once the holding time was complete, the reactor was decompressed and the treated bamboo residue was promptly taken out. The effect of hydrothermal treatment on the chemical properties of bamboo is incorporated in Table 1.

Composting system

The bench-scale composting systems were employed in this research. As shown in Fig. 1, composting was carried out in 250 ml perforated polystyrene vessels in which two layers of 1.5 g (dry weight) microbial seeds with 3.0 g (dry weight) starting composting mixture in the middle, were sandwiched between the two porous stratums of 5 g perlite (wetted with 15 mg pure water). The microbial seed was derived from the commercial compost (Wakayama Organic Productive Union, Japan). Prior to use, it was sieved (passed through 2 mm and retained on 1 mm mesh screen) and pre-incubated (27–60 °C) for five days with frequent mixing. This was done to guarantee reproducibility of gaseous emissions from the compost seed, since limited NH_3 and CO_2 productions were expected from the mixtures. The composting mixtures were prepared by adding either hydrothermally treated or raw bamboo residue to green kudzu with a mixing ratio that would produce a C/N ratio close to 25. Thus, the green kudzu and treated bamboo were mixed with 1.36:1.65 ratio and labeled "Treated" mixture, and the green kudzu and raw bamboo were mixed with 1.30:1.70 ratio and labeled "Control" mixture. The moisture content in both mixtures was adjusted to 65%, by adding distilled water. The other properties of the mixtures are shown in Table 2. The vessels were then sealed in 2-l jars and incubated to undergo composting process, including blank vessels that contained only perlite and microbial seeds. The temperature inside the incubation was room temperature during

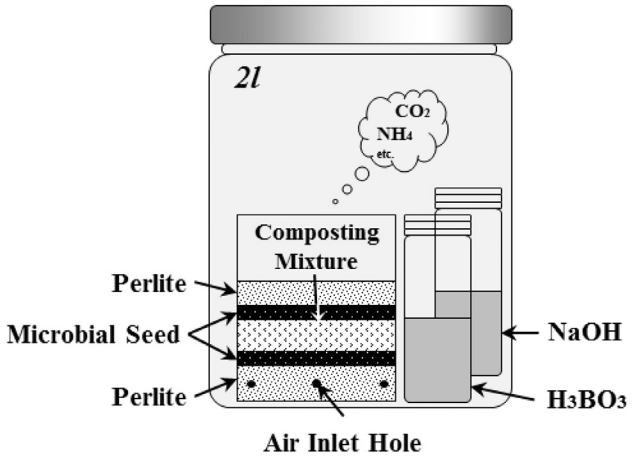

Fig. 1. Biometer jar for simulating aerobic composting.

Table 2
Starting composition of Treated and Control mixtures.

Parameters	Treated mixture	Control mixture
Mixing ratio[a]	1.36:1.65	1.30:1.70
Simple sugars[b], %	13.39	5.38
Hemicellulose[b], %	12.45	25.43
Cellulose[b], %	33.28	32.85
Lignin[b], %	25.21	17.85
Moisture content, %	65.00%	65.00%
pH	5.36 (0.05)	5.97 (0.04)
OM, %	95.11 (0.20)	95.17 (0.32)
Total C, %	47.29 (0.04)	45.16 (0.03)
Total N, %	1.82 (0.01)	1.71 (0.01)
C:N ratio	25.91	26.44

A (*B*), where *A* = mean and (*B* = standard deviation) with $n = 3$.
[a] Dry base.
[b] Values are estimated based on respective mixing ratios and the data in Table 1.

the first day before it was raised gradually to a set point of 60 °C during the next 3 days. Then, temperature of 60 °C was kept until the end of experiment. The perlite was used to ensure an aerobic condition in the vessels, as well as to prevent possible over-drying during incubation. In order to trap the NH_3 gas volatilized during composting, each jar was mounted with a glass vial containing 20 ml of (4% w/v) boric acid solution and a few drops of bromocresol green-methyl red ethanol indicator. A vial containing 20 ml solution of 2 N sodium hydroxide was also placed for trapping evolved CO_2. The traps were substituted at prefixed times, as indicated by the markers in the graphs. Six replicates were initially set-out for each composting mixture and three for the blank. Over the course of incubation, three vessels were withdrawn randomly from Treated and Control sets (on days 2, 6 and 10), and after careful brushing away the perlites and microbial seeds composted mixtures were subjected to pH analysis.

Analyses

The total carbon and nitrogen, before and after incubation, were determined using automatic high sensitive NC-analyzer (Sumigraph NC-220F, SCAS, Japan) based on 200 mg oven-dried samples. The pH was analyzed in 1:10 (w/v) composting mixture and distilled water solution following a 30-min shaking. Organic matter was determined by combustion of 3 g oven-dried sample at 550 °C for 2 h in a muffle furnace. The simple sugars (as glucose and xylose equivalent) in bamboo residue before and after hydrothermal treatment were estimated according to the method proposed by Yemm and Willis (1954). The hemicellulose, cellulose and lignin were determined following the procedures reported by Allen (1989). The amount of NH_3 gas trapped in boric acid solution was determined by back titration using 0.0025 M H_2SO_4 solution. The CO_2 collected in sodium hydroxide solution was measured by back titration with 1 N HCl to a phenolphthalein endpoint after adding excess $BaCl_2$. All results were corrected for gaseous emissions from microbial seeds i.e. blank. The statistical analysis of data was performed using the Data Analysis ToolPack of the Excel (Microsoft Office 2010). A *t*-Test (assuming the two-tail and 95% confidence level) was used for testing significant differences of the results obtained.

Results and discussions

The pH evolution

Initially, the pH values in both composting mixtures were acidic, 5.41 and 5.97 in the Treated and Control mixtures, respectively. The slight difference in pH values was due to the presence of organic acids formed normally during hydrothermal treatment of bamboo residue. Nevertheless, the pH in both composts increased rapidly and alkaline values ranging between 8.30 and 8.40 were detected after two days of incubation. This could be due to the rapid decomposition and subsequent release of ammonia from the nitrogenous compounds in green kudzu. The high pH values were observed until the day 10. Then, the pH in both mixtures decreased and became nearly neutral (7.29–7.51) by the end of experiment.

CO_2 production

Monitoring the dynamic of CO_2 production during composting process is useful because it directly reflects the availability of organic carbon compounds for microorganisms, which is important for immobilization of inorganic nitrogen and subsequent reduction of NH_3 volatilization (Reinertsen et al., 1984; Li et al., 2013a,b). The patterns of CO_2 production during composting of Treated and Control mixtures are shown in Fig. 2a,b. As summarized in Table 2, the initial amount of simple sugars i.e. readily-available source of carbon in Treated mixture was higher than in Control mixture due to the effect of hydrothermal treatment on bamboo residue. Previous studies have shown that the flush of CO_2 at the early stage of decomposition is attributed to rapid catabolism of readily-available carbon compounds (Knapp et al., 1983). A relatively higher initial microbial activity, characterized by significantly higher ($p < 0.05$) CO_2 production rate on the second day of incubation, was observed for Treated mixture (Fig. 2a). In fact, the higher microbial activity in Treated mixture was also apparent visually: the white colored microorganisms in Treated mixture appeared earlier and was more intense than in Control mixture (unpublished results). The white microorganisms appeared were expected to be actinomycetes because according to the producer's claim, the compost that was used as microbial seeds in this research contained approximately 21 million of actinomycetes per gram of compost. A similar phenomenon was observed by Matsumura et al. (2010) during composting of rabbit food supplemented with lard. This was not hard to expect because rabbit food and green kudzu are very similar in composition. More so, the higher CO_2 production rate in Treated mixture continued until the twelfth day of incubation. These results seem to indicate that after all the readily-available carbon were utilized intermediately-available carbon sources such as cellulose became shortly available and continued supporting the activity of microorganisms at the later stage of composting. According to Fig. 2b, the cumulative CO_2 production in Treated mixture was 1101.77 mg g^{-1} d.m. compared to 941.53 mg g^{-1} d.m. in Control mixture, which correspond to 63.12% and 56.95% of the total mass of organic carbon presented in the mixtures, respectively.

NH_3 volatilization

The behaviors of NH_3 volatilization during composting of Treated and Control mixtures showed similarity in pattern but as expected, remarkable difference in size (Fig. 2c,d). Specifically, with the increase of process temperature, and when the pH values were >8, NH_3 volatilization rates in both mixtures increased sharply and reached a peak at day 4 (Fig. 2c). Then, NH_3 volatilization rates started to decrease and nearly no more losses were observed from day 9 onwards. In both cases, the peak of NH_3 volatilization rates coincided with the highest value of process temperature (60 °C). High temperature and pH, in fact, have been identified as the two main factors influencing NH_3 volatilization during composting of a given organic waste (Pagans et al., 2006), because solubility of NH_3 at such elevated condition is greatly reduced within the substrate. For example, in the experiment of Sikora (1999), NH_3 solubility decreased by 30% when temperature increased from 40 to 55 °C at high pH, causing an increase of NH_3 concentration in the exhaust

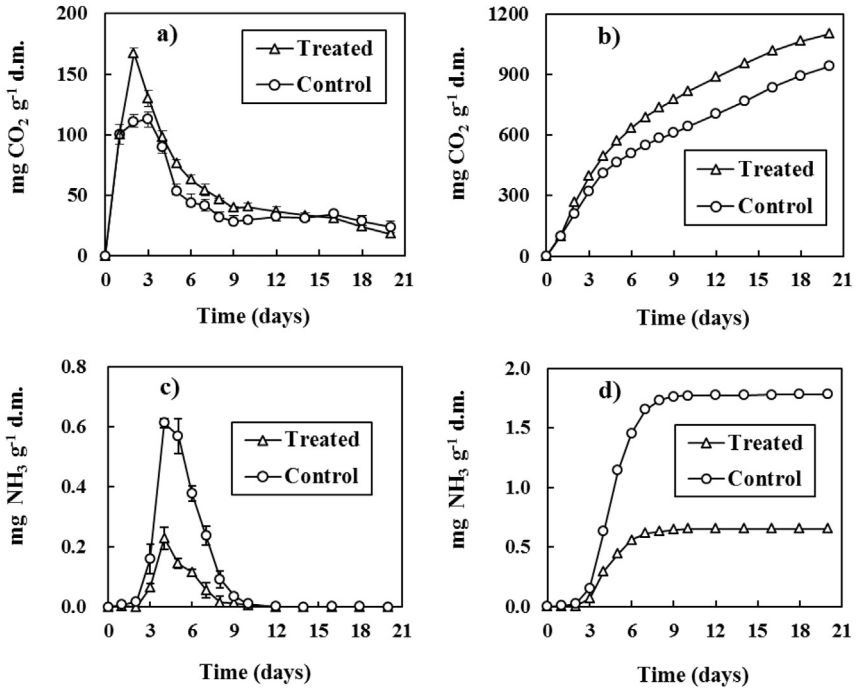

Fig. 2. Changes of CO_2 production (a), cumulative CO_2 production (b), NH_3 volatilization rate (c) and cumulative NH_3 volatilization (d) during composting process of treated and control mixtures (horizontal bars indicate 95% confidence intervals with $n = 3–6$).

gas of the composting process. In this experiment as well, NH_3 volatilization rates increased notably when temperature was increased from 37 to 60 °C during days 2–4. However, NH_3 volatilization rate in Treated mixture showed significantly lower ($p < 0.05$) peak value (0.230 mg g^{-1} d.m. d^{-1}) compared to that in Control mixture (0.613 mg g^{-1} d.m. d^{-1}), although the pH value in the mixtures did not differ considerably. These results suggest that the high amount of simple sugars initially present in Treated mixture promoted microbial activity to immobilize more inorganic nitrogen during the intensive stage of organic nitrogen decomposition, which in turn reduced the peak of NH_3 volatilization. Li et al. (2013b) emphasized that immobilization of inorganic nitrogen may end (and thus NH_3 volatilization rate may increase) when the carbon sources are depleted. Nevertheless, after the initial peak on day 4, the plot of NH_3 volatilization in Treated mixture showed immediate decrease, suggesting that the release of intermediately-available carbon sources supported microorganisms to continue immobilization of inorganic nitrogen in the later stage of process. According to Fig. 2d, cumulative NH_3 volatilization during 20 days of incubation in Treated mixture was 0.653 mg g^{-1} d.m., while in Control mixture it reached 1.781 mg g^{-1} d.m., which corresponds to 3.37% and 9.61% of the total mass of nitrogen contained in each gram of Treated and Control mixtures, respectively. The large difference in NH_3 volatilization was also reflected by the significant difference ($p < 0.05$) in C/N ratio of final products in the mixtures. As elemental analysis showed, the C/N ratio after 20 days of incubation in Treated mixture was 19.47 compared to 23.89 in Control mixture. This again confirms the effectiveness of the addition of hydrothermally treated lignocellulose in reducing NH_3 volatilization during composting process.

Feasibility for practical use

It is well known that the high rate of NH_3 volatilization during composting process can reduce the quality of the final product as an organic fertilizer. Various strategies have been proposed by other researchers to minimize NH_3 volatilization during the composting of organic wastes. The results of this bench-scale research showed that addition of hydrothermally treated lignocellulose reduced NH_3 volatilization by about 3 times. The hydrothermal treatment in general, is a process that uses high temperature and high pressure steam to upgrade various types of biomass waste into fuels and/or various value-added products (Jing, 2014). The technology has recently been gaining popularity because the operation is simple and flexible and furthermore, expensive reactor systems are not necessary since no corrosive catalysts are used. Nevertheless, the hydrothermal treatment system requires energy source for generating steam to be applied to the reactor during the treatment process. It is therefore, important to discuss the cost of hydrothermal treatment of lignocellulose for NH_3 volatilization reduction during composting of organic wastes. According to Rynk (1992), the average C/N ratio of the most common livestock manures such as swine, turkey and cattle is 14, 16 and 19, respectively. Assuming a C/N ratio of 25–30 for starting composting mixture, the amount of lignocellulose necessary (for example, in form of rice straw with C/N ratio of 112) to be added to 1 Mt of turkey, cattle and swine manure would be approximately 1.0–1.5 Mt, 0.7–1.1 Mt and 0.4–0.8 Mt, respectively. The large-scale hydrothermal treatment system (with 5 m^3 inner volume) developed in Yoshikawa laboratory of Tokyo Institute of Technology, for example, requires approximately 0.5 Mt of steam or 44 l of diesel fuel (with heating value of ~35 MJ/kg) to treat 1 Mt of biomass at 180 °C, 30 min. In Japan, the current price of diesel fuel is about 134 JPY per liter (≈1.31 US$). Thus, the cost of hydrothermal treatment of lignocellulose for 1 Mt of swine, turkey and cattle manures (dry base) is approximately 5896–8844 JPY, 4127–6485 JPY and 2358–4716 JPY, respectively. Although the hydrothermal treatment of lignocellulose adds an extra cost to the low value-added product, compost, it may still be advantageous over the other proposed methods such as addition of chemical absorbents. Because, unlike the chemical additives, the lignocellulosic residues are widely available in nature, and in many cases are already being used on-site. The cost of the

hydrothermal treatment of lignocellulose could also be comparable to that of molasses addition, if the initial cost of the facility is not considered. For example, Liang et al. (2006) added 1.5 kg of molasses and 9.5 kg wheat straw to 4.5 kg dairy manure (dry base) and the nitrogen loss during composting was reduced by 2 times (from 24.6% to 12.1%). Currently raw molasses is being exported at an average f.o.b. price of 140–200 US$ or 14,329–20,929 JPY per 1 Mt (UM Trading, 2014). Thus, to achieve the same level of nitrogen loss reduction, the cost of molasses application for 1 Mt of dairy manure composting would approximately be 4771–6969 JPY, which is a similar to the cost of hydrothermal treatment of lignocellulose i.e. wheat straw. In addition, hydrothermal treatment or addition of lignocellulose to compost mixture will positively affect the stability of compost that is important for shortening the composting time.

Conclusions

A new strategy for reducing NH_3 volatilization during composting of organic waste rich in nitrogen was tested. The addition of hydrothermally treated lignocellulose (180 °C, 1.0 MPa, 30 min) to composting mixture was very effective in reducing NH_3 volatilization during the bench-scale composting experiment. The effect was mainly due to the presence of high amount of simple sugars in treated lignocellulose, which promoted microbial activity to immobilize more inorganic nitrogen during intensive decomposition of nitrogenous compounds. As a result, NH_3 volatilization reduced from 9.61% in Control to 3.37% in Treated mixture. The difference in NH_3 volatilization was also reflected by the significant difference ($p < 0.05$) in C/N ratio of the final compost products. The addition of hydrothermally treated lignocellulose also enhanced the overall biodegradation rate of organic matter in the composting mixture.

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